This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.



COMPOSITESPart B: engineering

Composites: Part B 30 (1999) 227-231

Electromagnetic interference shielding using continuous carbon-fiber carbon-matrix and polymer-matrix composites

Xiangcheng Luo, D.D.L. Chung*

Composite Materials Research Laboratory, State University of New York at Buffalo, Buffalo, NY 14260-4400, USA

Received 1 December 1997; accepted 6 November 1998

Abstract

A carbon-matrix composite with continuous carbon-fibers was found to be an excellent electromagnetic interference (EMI) shielding material with shielding effectiveness 124 dB, low surface impedance and high reflectivity in the frequency range from 0.3 MHz to 1.5 GHz. The shielding effectiveness of polymer-matrix composites with continuous carbon-fibers was less and that of polymer-matrix composites with discontinuous fillers was even less. The addition of 2.9 vol.% discontinuous 0.1 μ m diameter carbon-filaments between the layers of conventional 7 μ m diameter continuous carbon-fibers in a composite degraded the shielding effectiveness. The dominant mechanism of EMI shielding for both carbon-matrix and polymer-matrix continuous carbon-fiber composites is reflection. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: A. Carbon-fiber; A. Carbon-carbon composites (CCCs); A. Polymer-matrix composites (PMCs); Electromagnetic interference shielding

1. Introduction

Electromagnetic interference (EMI) shielding is receiving increasing attention in electronic and communication industries because of devices becoming increasingly sensitive, dense and abundant. Composites with discontinuous conducting fillers, such as metal particles, metal flakes, carbon particles and carbon-fibers, are widely used for EMI shielding [1–10]. Although these composites are not strong enough for most structural applications, they are attractive because of their processability by injection molding and other commonly used polymer processing methods. For these composites, the EMI shielding effectiveness increases with increasing volume fraction of the filler and with increasing aspect ratio of the filler.

The shielding effectiveness of various polymer-matrix composites with discontinuous fillers were previously compared [1–10], but comparison has not been made between those with continuous fiber fillers and those with discontinuous fillers. Comparison has also not been made between polymer-matrix and carbon-matrix composites although it was suggested based on theory that the carbon-matrix composite is superior in shielding to the polymer-matrix composite by an insignificant amount [11]. As the shielding effectiveness varies with the testing configuration,

Structural composites mostly use continuous rather than discontinuous fillers as reinforcement. A structural composite that is capable of EMI shielding is particularly needed for aircraft, which houses electronics. If the shielding is mainly because of reflection, the composite is low in surface impedance and is thus valuable for lightning protection, which is also needed for aircraft. Carbon-matrix composites with continuous carbon-fibers (called carbon-carbon composites) are used for aerospace structures that require high temperature resistance. This article provides the first experimental study of the EMI shielding effectiveness of a carbon-carbon composite, which was found to be an excellent shielding material - even better in shielding effectivethan continuous carbon-fiber polymer-matrix composites. Previous reports on the shielding effectiveness of continuous carbon-fiber polymer-matrix composites were mainly in the frequency range from 1 to 12 GHz [12-14]. More detailed studies regarding the EMI shielding effectiveness of polymer-matrix composites have also been conducted in relation to the laminate properties, the fiber orientation and anisotropy of laminates, and the angle and polarization of the incident wave [15]. The EMI shielding of

comparison of effectiveness values determined by using different testing configurations is not reliable. Therefore, this article emphasizes comparison of results obtained using the same testing configuration for polymer-matrix and carbon-matrix composites.

^{*} Corresponding author. Tel.: 001 716 645 2593; fax: 001 716 645 3875.

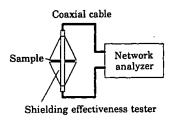


Fig. 1. Set-up for electromagnetic shielding effectiveness measurement.

polymer-matrix and carbon-matrix composites in a lower frequency range (0.3 MHz-1.5 GHz) is addressed in this article as a result of the relevance of this range to radio frequency devices, such as wireless communication devices, which are a main source of interference to digital devices.

Various electrically conductive fillers, such as silvercoated ceramic microballoons (discontinuous) and metal mesh (continuous), were added to continuous fiber composites for enhancing the EMI shielding effectiveness [16,17]. Experimental and theoretical investigation of the EMI shielding effectiveness has also been done on intrinsically conductive polymers in the frequency range from 1 MHz to 3 GHz [18]. The microballoons are effective for enhancing the shielding effectiveness of a continuous glass fiber polymer-matrix composite [16]; since glass fibers are not conducting, this result is expected. However, when continuous carbon-fibers, which are conducting, are used in place of the glass fibers, the effect of a conducting discontinuous filler is expected to be much less. This article provides the first study of the effect a discontinuous conducting filler on the shielding effectiveness of a continuous carbon-fiber composite. The discontinuous filler used was carbon-filaments of diameter 0.1 µm (much smaller than the diameter of 7-12 µm for a conventional carbon-fiber), owing to the skin effect (phenomenon in which electromagnetic radiation at high frequencies interacts only with the near surface region of a conductor) causing the small diameter to be attractive. In this article, "filaments" refer to those of diameter less than 1 \(\mu\mathrm{m}\) and "fibers" refer to those of diameter greater than 1 µm. These filaments were previously shown to be useful for improving the vibration damping ability [19]. This work unexpectedly shows that the filaments do not improve the shielding effectiveness of a continuous carbon-fiber composite. They even degrade the shielding effectiveness.

2. Experimental methods

2.1. Materials

The carbon-carbon composite, kindly provided by Sigri Great Lakes Carbon Corp. (Union, NJ) under the grade designation of CC 1501G, was in the form of a sheet comprised of continuous carbon-fiber roving fabric (90° biaxial weave) and was produced by lamination and compression. The heat treatment temperature used in production was 2000°C. The bulk density was 1.40–1.45 g/cm³; the open porosity was 20%–25%; the tensile strength was about 382 MPa. The composite was cut into different shapes for various measurements described later.

Polymer-matrix composites with crossply continuous carbon-fibers (10E, Torayca T-300, 6K, untwisted, UC-309 sized, diameter = $7 \mu m$, tensile strength = 3.1 GPa, tensile modulus = 221 GPa and density = 1.76 g/cm^3) as reinforcement at 47 vol.% and epoxy (976, $T_g = 232$ °C, density = 1.28 g/cm³) as matrix were made by hot pressing prepreg tapes (ICI Fiberite, Tempe, AZ) in a crossply [0°/ 90°] configuration in a steel mold at 160°C and 3.0 MPa for 2 h. Discontinuous amorphous carbon-filaments (ADNH, from Applied Sciences Inc., Cedarville, Ohio) of diameter 0.1-0.2 µm and length at least 100 µm and with a naturally bent morphology were made into sheets by vacuum filtration. The electrical resistivity $4.1 \times 10^{-4} \Omega m$ for the filaments was calculated from the volume electrical resistivity of filament compacts, as measured by the four-probe method [20]. A filament sheet was optionally introduced into every interlaminar region of a composite prior to hot pressing, such that the filaments occupied 2.9% of the volume of the composite after hot pressing. This volume fraction is much higher than that in [19]. The number of fiber laminae were 19 and 12 for composites without and with filaments respectively. These numbers were chosen so as to make the different composites similar in thickness.

Polymer-matrix composites with various discontinuous fillers (including the carbon-filaments) and polyether

Table 1
Electrical resistivity and attenuation upon transmission and reflection of continuous carbon-fiber composites

Matrix	Filler	Number of carbon- fiber laminae ^b	Resistivity, through thickness direction $(\Omega.m)$	Resistivity, in- plane direction $(\Omega.m)$	Attenuation upon transmission (dB)*	Attenuation upon reflection (dB)	Thickness for attenuation measurement (mm)
Carbon	Fibers		/	2.16×10^{-5}	124.7 ± 6.9	0.02	2.40
Ероху	Fibers	19	3.5×10^{-3}	7.2×10^{-5}	114.8 ± 9.4	0.05	2.08
Ероху	Fibers + filaments	12	4.5×10^{-2}	9.1×10^{-4}	98.3 ± 11.9	0.07	1.90

^{*} Same as the EMI shielding effectiveness. Value before " ± " is the average attenuation. Value after " ± " is the average range of variation.

^b Chosen to make the thicknesses (last column) similar for different composites.

sulfone (PES, $T_{\rm g}=220^{\circ}{\rm C}$, density = 1.37 g/cm³, particle size = $100-150~\mu{\rm m}$) as matrix were fabricated by forming a mixture of the polymer power and the filler and subsequent hot pressing at 310°C and 13.4 MPa for about 30 min [10].

2.2. Electromagnetic transmission/reflection measurements

The shielding effectiveness was measured using the coaxial cable method. The set-up as illustrated in Fig. 1 consisted of an Elgal (Israel) SET 19A shielding effectiveness tester, which was connected to a Hewlett-Packard (HP) 8752C network analyzer. An HP 85032B type N calibration kit was used to calibrate the system. Then standard attenuators with a total attenuation 130 dB were tested to ensure that the dynamic measurement range up to 130 dB is valid for all sample measurements. The frequency was scanned from 0.3 MHz to 1.5 GHz and 201 data points were taken in reflection and also in transmission. The average of SE value and the range of SE variation of these 201 data points within the measured frequency range were calculated. One sample of each type was measured at least five times. The average SE value and variation range of SE within the frequency range for all measurements of each sample were separately averaged and indicated in Table 1. The attenuation under transmission and that under reflection were measured. The former is equivalent to the shielding effectiveness. The samples were in an annular form with outer diameter 97 mm and inner diameter 32 mm. The thicknesses of the samples are listed in Table 1.

2.3. Resistance/impedance measurements

The DC electrical resistivity in a fiber direction in the plane of the laminate was measured by a Keithley 2002 Multimeter using the four-probe method and silver-epoxy electrically conducting paste for the electrical contacts. The specimens were rectangular, of length 15-47 mm, width 1.2-6.1 mm and thickness 2.8-3.3 mm. The resistivity of the samples in the through-thickness direction was also measured by the four-probe method, with the two current probes formed by copper wire in the form of loops with diameter 22.5 mm attached with silver-epoxy to the opposite faces in the plane of the composite sheet and the two voltage probes in the form of dots attached with silverepoxy to the centers of the loops. The same samples for in-plane resistivity measurement were used for the AC impedance measurement by a QuadTech 7600 RLC Meter, in which the frequency was scanned from 10 Hz to 2 MHz and 200 data points for each frequency scan were collected. The surface impedance of the materials Z_l was measured from 0.3 MHz to 1.5 GHz by the same set-up which was used for the reflection measurement and was calculated using the equation

$$Z_{i} = Z_{0} \sqrt{\frac{1 + |S_{11}|^{2} + 2|S_{11}|\cos\varphi}{1 + |S_{11}|^{2} - 2|S_{11}|\cos\varphi}},$$

where S_{11} is the reflection coefficient (i.e., the ratio between the voltage of reflected electromagnetic wave and that of source electromagnetic wave), φ is the phase angle and Z_0 is the characteristic impedance of the instrument, which is 50Ω .

3. Results and discussion

The EMI shielding effectiveness (SE) is composed of three portions, namely reflection, absorption and multiple reflections. Reflection is as a result of the impedance mismatch between air and the sample at the frequency of interest; the absorption is because of the energy dissipation while electromagnetic wave interacts with the material; the multiple reflections are as a result of the inhomogeneity within the material. The higher the SE value in decibel, the less energy passes through the sample.

$$SE(dB) = 10\log_{10}(I_i/I_t)$$

where I_i the intensity of the incident beam and the I_t is the intensity of the transmitted beam.

The EMI shielding effectiveness of the carbon-matrix and epoxy-matrix composites is shown in Table 1, along with the DC resistivity. The higher the resistivity, the lower the shielding effectiveness and the higher the attenuation upon reflection. The carbon-matrix composite exhibits lower resistivity than the epoxy-matrix composites. The low resistivity of the carbon-matrix composite is attributed to the much lower resistivity of the carbon matrix compared to the epoxy matrix, which is insulating. Similarly, the high shielding effectiveness of the carbon-matrix composite compared to the epoxy-matrix composites is attributed to the carbon-matrix. The introduction of the carbon-filaments between the fiber layers does not improve the electrical conductivity or the shielding effectiveness of the epoxymatrix composite. The composite with carbon-filaments has a lower SE value as well as higher resistivities in both in-plane and through-thickness directions than that without the filaments. Under an optical microscope, we observed carbon-filament-epoxy interlayers carbon-fiber laminae. The presence of the carbon-filaments, which are discontinuous and not particularly conductive anyway, caused the observed large increases in the through-thickness and in-plane resistivities.

The low attenuation upon reflection for all the composites (Table 1) means that reflection dominates the shielding mechanism. In other words, most of the incident energy is reflected back to the transmitter. This is consistent with the high conductivity of these composites. The carbon-carbon composite has the highest SE value (124 dB) and the least attenuation upon reflection (0.02 dB) among the composites. Fig. 2 shows the SE variation with frequency for these three composites. The SE values for the epoxy-matrix composites with and without carbon-filaments decrease at low frequencies. The impedance measurement indicates a

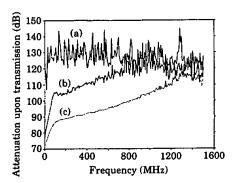


Fig. 2. Attenuation upon transmission vs. frequency for composites with continuous carbon-fiber (a) Carbon-carbon composite. (b) Epoxy-matrix carbon-fiber composite. (c) Epoxy-matrix carbon-fiber carbon-filament composite.

similar trend (Fig. 3). The carbon-carbon composite has the most severe skin effect; its impedance increases most abruptly with the increase in frequency. The impedance values of the epoxy-matrix composites also increase with frequency, but the abrupt increase occurs at higher frequencies. The low value of the attenuation upon reflection (Table 1) and the consistency between the transmission and impedance measurements show that reflection is the dominant mechanism for EMI shielding using continuous carbon-fiber carbon-matrix and polymer-matrix composites. The dominance of reflection was previously reported for continuous carbon-fiber polymer-matrix composites [12–14].

The surface impedance values of the three composites of Table 1 in the measured frequency range are all below 3 Ω . Among these composites, the carbon-matrix composite has the lowest surface impedance – about the same as that of the solid copper at each corresponding frequency, whereas the epoxy-matrix composite with carbon-filaments as interlaminar filler has the highest surface impedance at each corresponding frequency. This trend is consistent with the results of other electrical measurements (Table 1). The strong reflectivity and low surface impedance suggest that the carbon-matrix and polymer-matrix composites are also

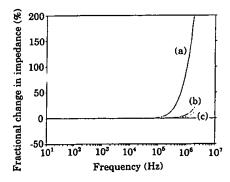


Fig. 3. Impedance vs. frequency for composites with continuous carbon-fibers (a)Carbon-carbon composite. (b) Epoxy-matrix carbon-fiber composite. (c) Epoxy-matrix carbon-fiber carbon-filament composite.

effective for lightning protection, electrostatic dissipation and use as microwave waveguides.

The SE values of PES-matrix composites of the same thickness (about 2.8 mm) and with various discontinuous fillers, all tested at 1-2 GHz using the same shielding effectiveness tester (Elgal SET 19A), are listed in the Table 2. The carbon-filaments in Table 2 are the same as those used in this work as an interlaminar filler. As shown in Table 2, they are less effective than nickel particles (1-5 µm), nickel fibers (2 µm diameter) and nickel filaments (0.4 µm diameter), in spite of their small diameter and the skin effect. The composite with nickel filaments as filler has the highest SE value (87 dB) among all the composites in Table 2. This is believed to be because of the small diameter in conjunction with the skin effect, as shown when this composite is compared with that having SE value 58 dB and nickel fibers of a much larger diameter (2 µm) at the same volume fraction [21]. Using polyimide siloxane as the matrix, comparison between nickel particle and silver particle composites shows that nickel particles are more effective for shielding than silver particles. This is probably because nickel is magnetic. All the composites with discontinuous fillers (Table 2) have lower SE values than the composites with the continuous carbon-fibers (Table 1).

Owing to the high shielding effectiveness of continuous carbon-fiber composites compared to that of composites with discontinuous fillers, the addition of a discontinuous interlaminar filler to a continuous carbon-fiber composite is not expected to have much positive influence on the shielding effectiveness. The influence turns out to be even negative for the addition of carbon-filaments as a discontinuous interlaminar filler, partly because of the relatively large volume fraction of carbon-filaments (2.9 vol.%) between the carbon-fiber laminae in this work compared to the low volume fraction (0.6 vol.%) in Ref. [19].

4. Conclusion

Composites with continuous carbon-fibers have better EMI shielding effectiveness than those with discontinuous fillers. However, a continuous carbon-fiber composite with a carbon-matrix is more effective for shielding, more reflective, and more conductive than that with an epoxy matrix, reaching an EMI shielding effectiveness of 124 dB at 0.3 MHz–1.5 GHz. The introduction of 2.9 vol.% discontinuous 0.1 μm diameter carbon-filaments to an epoxymatrix composite with continuous 7 μm diameter carbon-fibers degrades the EMI shielding effectiveness. The dominant mechanism of EMI shielding for these continuous carbon-fiber structural composites is reflection.

Acknowledgements

This work was supported in part by Defense Advanced Research Projects Agency. The authors are grateful to

Table 2
EMI shielding effectiveness at 1-2 GHz for PES-matrix composites (thickness about 2.8 mm) measured using the same shielding effectiveness tester^a

Filler	Vol.%	EMI shielding effectiveness (dB)	Ref. No.	•
Al flakes (15 \times 15 \times 0.5 μ m)	20	26	[22]	
Steel fibers (1.6 μm dia. × 30-56 μm	20	42	[22]	
Carbon-fibers (10 μm dia. × 400 μm)	20	19	[22]	
Ni particles (1-5 μm dia.)	9.4	23	[22]	
Ni fibers 20 μm × 1 mm)	19	5	[21]	
Ni fibers (2 μ m × 2 mm)	7	58	[21]	
Carbon-filaments (0.1 μm dia. × > 100 μm)	7	32	[21]	
Ni. Filaments (0.4 μm dia. × > 100 μm)	7	87	[21]	

^{*41} dB at 5.7 vol.%, compared to 1.5 dB at 4.9 vol.% for silver particles (0.8-1.35 µm), for composites with a polyimide siloxane matrix [22].

Professor J.J. Whalen of the State University of New York at Buffalo for helpful discussions.

References

- Murthy M. 4th Int. SAMPE Electronics Conference, (Electronic Materials-Our Future), edited by Allred RW, Marinez RJ, Wischmann KB, Vol. 4 1990, pp. 806-818.
- [2] Bell JAE, Hansen B. 24th Int. SAMPE Technical Conference. 1992; T902-T911.
- [3] Bigg DM. Polym Compos 1983;4(1):40-46.
- [4] Bigg DM. Polym Compos 1987;8(1):1-7.
- [5] Dixon DS, Masi JV. SAMPE J 1989;25(6):31-37.
- [6] Ramadin Y, Jawad SA, Musameh SM, Ahmad M, Zihlif AM, Paesano A, Martuscelli E, Ragosta G. Polymer International 1994;34(2):145– 150.
- [7] Jana PB, Mallick AK, De K. IEEE Trans Electromagnetic Compatibility 1992;34(4):478-481.
- [8] Jana PB, Mallick AK, De K. Composites 1991;22(6):451-455.
- [9] James K, Nard S. 3rd Int SAMPE Electronics Conf, 1989, pp. 1125-

- [10] Shui X, Ph.D. dissertation, State University of New York at Buffalo, 1996, p. 48.
- [11] Gaier JR, NASA-TM-103677, 1/1/1990.
- [12] Jana PB, Mallick AK. J Elastomers and Plastics 1994;26(1):58-
- [13] Atkins DJ, Miller JA, Sanders JD. 8th Int. Conf. Electromagnetic Compatibility, Electronics Division, Institution of Electrical Engineering, London, 1992, pp. 100-107.
- [14] Jaworske DA, Gaier JR, Hung CC, Banks BA. SAMPE Q 1986;18(1):9-14.
- [15] Lin Ming-Shing, Chen Chun Hsiung. IEEE Transactions on Electromagnetic Compatibility 1993;35(1):21-27.
- [16] Olivero DA, Radford DW. SAMPE Q 1997;33(1):51-57.
- [17] Gan YX, Jang BZ, 2nd Int. Conf. Composites Engineering, 1995, pp. 243-244.
- [18] Colaneri, Nick F, Shacklette, Lawrence W. IEEE Transactions on Instrumentation and Measurement 1992;41(2):291-297.
- [19] Hudnet SW, Chung DDL. Carbon 1995;33(11):1627-1631.
- [20] Shui X, Ph.D. dissertation, State University of New York at Buffalo, 1996, p. 29.
- [21] Shui X, Chung DDL. J Electron Mater 1995;24(2):107-113.
- [22] Li L, Chung DDL. Composites 1994;25(3):215-224.